THE ANALYSES OF SOME MASTODON AND MAMMOTH TUSKS

by

WILLIAM EDWARD MOLING

A. B., University of Missouri, 1925

A THESIS

submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

KANSAS STATE COLLEGE

OF AGRICULTURE AND APPLIED SCIENCE

1933

TABLE OF CONTENTS

INTRODUCTION

The original objective of this work was to determine the chemical composition of mastodon and mammoth tusks and their matrices; but after several determinations had been made, it became evident that the time alloted to the work would not be sufficient for solving so extensive a problem. Therefore, the work has been limited to the chemical analysis of four different samples of mastodon and mammoth tusks.

No literature pertaining to fossilized tusks was found, but a detailed account of the chemical composition of fossilized bones is obtainable[1]. Although there is a marked similarity between bones and tusks, they are not identical, and data pertaining to the one do not necessarily apply to the other. A few more scattering analyses of fossil bones are to be found in the literature, but according to Rogers[2], they are incomplete and of doubtful value, because the homogeneity of the material was not determined by microscopic investigation prior to the analyses and there was no guarantee of the purity of the materials tested.

Four samples of fossilized material (tusks) were analyzed in this investigation. For the sake of clarity they will be designated in this paper as samples A, B, C, and D.

Each sample was prepared for analysis by grinding in a mortar until sufficiently fine. Samples A, B, and C

were passed through a 100-mesh sieve, and sample D through an 80-mesh sieve.

Portions of each uniformly-mixed sample were used for the analyses.

Moisture determinations were made in aluminum dishes with lids, heating each sample in a drying oven at 110°C. to constant weight.

Protein determinations were made by the Kjeldahl process.

Loss of Weight on Ignition was found by igniting weighed quantities of the sample to constant weight in small platinum crucibles, using a Meker flame.

Insoluble Residue determinations were made by dissolving two-gram samples, after ignition to destroy organic matter, with two successive treatments of aqua regia, evaporating the mixture each time to dryness, and baking the residue on a hot plate for two hours. The residue was then warmed in dilute HCl, the mixture filtered, and the filter paper and contents ignited to constant weight.

Carbon dioxide determinations were made by treating weighed samples with dilute (CO_2 saturated) HCl, using a special type of apparatus, and measuring the volume of saturated NaCl solution displaced by the carbon dioxide. The volume of carbon dioxide was corrected to standard conditions of temperature and pressure (0°C. and 760 mm. Hg).

Combustions of the organic matter were made with absorption of carbon dioxide and water. The carbon dioxide included that obtained from the carbonates as well as that from the burning of the carbon. The water included moisture of hydration in addition to that obtained from the burning of the hydrogen of the organic matter.

Calcium, iron, and phosphate determinations were made upon aliquot portions of nitric acid solutions containing known weights of the samples. Two different methods were used for the determination of calcium: (1) the McCrudden method[3] designed for the determination of calcium in the presence of iron, aluminum, magnesium, and phosphates; and, (2) a method by Cox and Dodds[4] making use of a composite reagent for precipitating the calcium as oxalate in the presence of phosphates.

Phosphate determinations were made by the volumetric molybdate method.

Non-nitrogenous organic matter was determined by subtracting the total weights of proteins, carbon dioxide (from carbonates), and moisture of hydration from the loss of weight on ignition.

Thus the purpose and general procedure have been briefly explained. Attention may now be directed to the individual samples and their compositions.

ANALYSES OF THE SAMPLES

Although a number of similar tests were made on each one of the samples, no general scheme of analysis was followed for all of the samples.

A discussion of the individual samples will now be given.

Sample A

The sample was a fragment of a mastodon tusk, at least 25,000 years old, found in the Smoky Hill Valley near Delphos, Kansas. The material was a chalk-like, almost white substance formed in concentric layers. After being finely ground, the material was so light and chalky in its consistency that it required considerable rubbing with the fingers to force the fine and somewhat adhesive powder through the 100-mesh sieve.

With the exception of small amounts of insoluble residue, the sample dissolved readily with effervescence when treated with nitric and hydrochloric acids, showing the presence of carbonates.

Analysis of Sample A and Ratios of Constituents

	Percentages	Molecular Ratios
Calcium Oxide	50.00	0.892
Phosphorus Pentoxide	34.50	0.243
Carbon Dioxide	7.40	0.168
Magnesium Oxide	0.30	0.007
Water (110°C.)	3.16	0.175
Insoluble Residue	0.38	
Organic Matter (not protein)	2.92	
Proteins (Kjeldahl - factor 6.35)	0.46	
Ferric Oxide	trace	
Total	99.12	

On combining the above metallic and non-metallic oxides into their probable combinations (on the basis of their ratios) they yield approximately the following formula:

$3\ Ca_3\ (PO_4)_2 \cdot 2\ Ca\ (CO_3, O) \cdot 2.16\ H_2O$, which falls within the limits of the general formula for collophane, the mineral substance of fossilized bone as found by A. F. Rogers in the analysis of about 300 samples. Collophane is represented by the following general formula:

$3\ Ca_3\ (PO_4)_2 \cdot n\ Ca\ (CO_3, F_2, SO_4, O) \cdot (H_2O)_x$. *

About 95 per cent of this sample is collophane.

Sample B

The sample was a fragment of a mammoth tusk found in gravel and loose material near Randolph, Kansas. The

* n = 1 - 2; x is a variable.

material differed considerably in appearance and consistency from the first sample. A cross section of the material showed three concentric layers: (1) an inner core about one inch in diameter; (2) a middle layer about one-half inch thick with several radial cleavages; and (3) a whitish outer layer about one-sixteenth inch thick. The crevices were stained with a dark substance which had filtered in from the surrounding gravel. The sample was easily broken into large splinters which had a mottled appearance on their surfaces, but not throughout the material itself. Not much difficulty was encountered in pulverizing the material in a porcelain mortar.

This sample dissolved readily, with effervescence, when treated with acids, quite the same as the first sample.

Analysis of Sample B and Ratios of Constituents

	Percentages	Molecular Ratios
Calcium Oxide	50.52	0.903
Phosphorus Pentoxide	34.07	0.240
Carbon Dioxide	6.10	0.139
Water (110°C.)	3.38	0.188
Insoluble Residue	0.22	
Protein (Kjeldahl - factor 6.35)	0.31	
Organic Matter (not protein)	3.91	
Ferric Oxide	0.05	
Total	98.56	

Combining the above data gives the formula:

$3\ Ca_3\ (PO_4)_2 \cdot 2.29\ Ca\ (CO_3,\ O) \cdot 2.35\ H_2O$, which

likewise falls within the general formula for collophane, the mineral constituent of fossil bone.

Sample C

The third sample resembled the first in general appearance, being nearly white in color and chalky in consistency. A number of the pieces were covered with shellac which had been used in preserving the sample. The shellac was removed with alcohol, and the sample was dried for several hours at room temperature before being ground.

Analysis of Sample C and Ratios of Constituents

	Percentages	Molecular Ratios
Calcium Oxide	48.80	0.871
Phosphorus Pentoxide	34.57	0.243
Carbon Dioxide	6.20	0.141
Water (110°C.)	3.92	0.218
Insoluble Residue	0.45	
Protein (Kjeldahl - factor 6.35)	0.50	
Organic Matter (not proteins)	4.92	
Ferric Oxide	trace	
Total	99.36	

Formula: $3\ Ca_3\ (PO_4)_2 \cdot 1.74\ CaCO_3 \cdot 2.69\ H_2O$, showing that 93.49 per cent of sample C is collophane.

Sample D

The fourth sample, a fragment of tusk belonging either to a mastodon or to a mammoth, was found in the sand of

Blue River near Rocky Ford, Kansas. The specimen differed in several respects from any of the three preceding ones. Its concentric layers, about one-sixteenth to one thirty-second of an inch in thickness, were much more finely knit, and the color was a light brown. The material was very much harder and tougher than the other samples, and apparently the outside horny layer of the tusk. It showed striations longitudinally as well as concentrically. This sample did not possess the chalky nature characteristic of the others, and passed through the sieve more readily when ground. It was much more difficult to grind than were the other three samples. These fragments were from the hard outer layer of a rather large tusk about 10 inches in diameter which had been weathered and leached considerably less than the other samples. Its composition had apparently been somewhat affected by its surroundings as it contained some alumina and much more iron than the other samples. An iron mortar was used for the grinding operation in preference to porcelain because of the severe treatment required. Any particles of non-oxidized iron that might have contaminated the sample during the grinding process were removed by means of a magnet.

Analysis of Sample D and Ratios of Constituents

	Percentages	Molecular Ratios
Calcium Oxide	37.80	0.674
Phosphorus Pentoxide	27.14	0.191
Carbon Dioxide	5.16	0.117
Insoluble Residue	0.40	
Moisture (110°C.)	5.53	0.307
Protein (Kjeldahl - factor 6.35)	19.00	
Ferric Oxide	2.86	
Total	97.89	

Formula: $3Ca_3(PO_4)_2 \cdot 1.83\ CaCO_3 \cdot 4.8H_2O$

Thus, 75.63 per cent of this sample consists of collophane. The organic matter in sample D as shown above represents only the nitrogenous material determined by the Kjeldahl method, which accounts very closely for the total amount of organic matter present.

SUMMARY AND CONCLUSIONS

The chemical compositions of four fossilized mastodon or mammoth tusks have been investigated.

No literature pertaining to fossilized tusks was found, although a good discussion of fossil bones was obtainable[1].

Samples A, B, and C showed great similarity in chemical composition and consisted of about 95-97 per cent collo-

phane, $3\ Ca_3\ (PO_4)_2 \cdot n\ CaCO_3 \cdot X\ H_2O$, while sample D consisted of 75.63 per cent collophane and 19 per cent organic matter. The following shows a summary of these compositions:

Substance	Samples A	B	C	D
Calcium Oxide	50.00	50.52	48.80	37.80
Phosphorus Pentoxide	34.50	34.07	34.57	27.14
Carbon Dioxide	7.40	6.10	6.20	5.16
Magnesium Oxide	0.30	none	none	none
Water (110°C.)	3.16	3.38	3.92	5.53
Insoluble Residue	0.38	0.22	0.45	0.40
Proteins (Kjeldahl - factor 6.35)	0.46	0.31	0.50	19.00
Organic Matter (not proteins)	2.92	3.91	4.92	-----
Ferric Oxide	trace	0.05	trace	2.86
Total	99.12	98.56	99.36	97.89

Approximate formulas of the four samples are:

A. $3\ Ca_3\ (PO_4)_2 \cdot 2\ Ca\ (CO_3,O) \cdot 2.16\ H_2O$

B. $3\ Ca_3\ (PO_4)_2 \cdot 2.29\ Ca\ (CO_3,O) \cdot 2.35\ H_2O$

C. $3\ Ca_3\ (PO_4)_2 \cdot 1.74\ Ca\ CO_3 \cdot 2.69\ H_2O$

D. $3\ Ca_3\ (PO_4)_2 \cdot 1.83\ Ca\ CO_3 \cdot 4.8\ H_2O$

The four samples of mastodon and mammoth tusks analyzed are composed of collophane, a phospho-carbonate of calcium which is the mineral constituent of fossilized bones in general and some phosphate rock, and the original mineral substance of living bone, together with small or larger

amounts of organic matter which is in part or almost wholly nitrogenous and which was in all probability a portion of the original organic matter of the living tusks.

ACKNOWLEDGMENT

The writer wishes to thank Dr. H. W. Brubaker whose helpful suggestions and able direction have made this work possible.

LITERATURE CITED

1. Rogers, A. F. Bulletin of Geol. Society of America, Vol. 35, pp. 535-556. September 30, 1924.

2. -------------- Bulletin of Geol. Society of America, Vol. 35, p. 538. September 30, 1924.

3. McCrudden, F. H. Journal of Biological Chemistry, Vol. 10, p. 187. August 3, 1911.

4. Cox, E. J. and M. L. Dodds. Industrial and Engineering Chemistry, Analytical Ed. October 15, 1932.

5. Osborn, Henry Fairfield. The Age of Mammals in Europe, Asia, and North America. New York. The MacMillan Co. 1910.